



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

UCRL-TR-226596

Separating Metallic Beryllium from Plutonium by Selective Dissolution with Ammonium Fluoride

Richard A. Torres

September 30, 2006

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Separating Metallic Beryllium from Plutonium by Selective Dissolution with Ammonium Fluoride

Richard A. Torres

Lawrence Livermore National Laboratory
Livermore, California 94551

September 30, 2006

Introduction

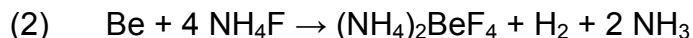
Plutonium metal is stabilized for long-term storage by calcining to produce PuO_2 . However, if beryllium is present, the calcined product may have a high neutron dose rate because of the ${}^9\text{Be}(\alpha, n){}^{12}\text{C}$ reaction in the finely divided oxide mixture. (At LLNL, inadvertent calcining of a mixture of ~500 g Pu / 50 g Be produced a neutron source of ~5 R/hr.) Therefore, for health physics reasons, we would like a convenient procedure to remove beryllium from plutonium with high selectivity.

Two reagents, sodium hydroxide and ammonium fluoride, were considered for aqueous processing. Each reagent selectively dissolves beryllium, which can be separated from the insoluble plutonium by decanting/filtering operations followed by water washes to remove the excess reagent. The washed plutonium is calcined for storage; the beryllium and wash fractions are solidified for disposal.

The respective dissolution reactions may be represented by:



and:



Krikorian and Bajao¹ have described the process which uses sodium hydroxide solutions to dissolve the beryllium. This process has several drawbacks:

- The reaction rate is slow below 50°C.
- A NaOH concentration greater than 20 wt% is necessary for appreciable solubility. (Be metal solubilities in NaOH determined in the present work are 0.05, 0.4, and 1.5 wt% Be for 20, 27.5, and 35 wt% NaOH, respectively.)
- Hydrogen bubbles have difficulty breaking through the viscous NaOH solvent, causing foaming and “boil over” problems.
- Periodic additions of the surfactant n-octanol mitigate the foaming problem, but constant operator attention is required.
- Filtration of the viscous NaOH solution is slow, and can take hours to finish.
- Concentrated NaOH filtrate/wash must be neutralized before liquid waste is solidified for ultimate disposal.

Our small scale experiments with beryllium alone suggested the NH_4F process offered some advantages over the NaOH method:

- The reaction is fast at room temperature.
- The NH_4F reaction is near stoichiometric. (The NaOH dissolution ceases once the concentration drops to ~20 wt% NaOH.)

- The NH_4F filtrate has a pH near 7, so no adjustment is required before liquid waste is solidified for ultimate disposal.
- The Be metal solubilities in NH_4F are larger than the corresponding NaOH solubilities. (Be metal solubilities are 0.05 and 1.3 wt% Be for 20 wt% NaOH and NH_4F , respectively. The Be solubility in 20 wt% NH_4F agrees with that found by Whitfield³ for a Be/Th/U alloy.)

Furthermore, tests with plutonium showed that the NH_4F process is much less subject to “boil over” problems. Even without a motor-driven stirrer, the foam was easily manageable by controlling the rate of ammonium fluoride reagent addition. No anti-foaming surfactant is necessary.

Results

The process was tested on one ~30 g sample, two ~100 g samples, and one ~200 g sample. After calcining the treated samples, neutron dose rates uniformly were ~1-2 mR/hr at the surface of the secondary cans.

Equipment

- 3-liter Pyrex beaker
- Steel tray for spill protection (Optional)
- Hot-plate (Automatic temperature feedback control is convenient, but not necessary.)
- Plastic- or glass-coated thermocouple for solution temperature measurement
- Stirrer motor with plastic propeller, plastic-coated shaft and controller. (Optional)
- Graduated cylinders
- Large plastic kitchen spatula
- Vacuum filtration system
- Buchner or bottle-top filter funnels
- Whatman #42 paper filters
- 1 liter disposable 0.45 μm membrane filtration units (Optional)

Specific brand names for the equipment used at LLNL are given in Reference 1. Comparable equipment from other vendors also may be used.

The use of a spill tray between the hot-plate and beaker severely reduces the efficiency of heat-transfer. This is a decided disadvantage in the NaOH process¹, which recommends heating the solution near 90°C. It is not as significant an issue with the NH_4F process, since temperatures of 60°C are sufficient to insure rapid and complete reaction. In fact, heating near boiling is discouraged with the NH_4F process, since the beryllium can reprecipitate as $\text{Be}(\text{OH})_2$ under these conditions.²

The spill tray is not really necessary, since it is easy to control the reaction rate. Since the reaction is near stoichiometric, 20 mL of 40% NH_4F will produce ~1.5 liters of hydrogen gas at 50°C. Therefore, for liquid volumes less than 1.5 liters in a 3-liter beaker, as long as the ammonium fluoride reagent is added in no greater than ~20 mL increments, the solution will not foam over.

Over time, plutonium shavings (originally in thin strips) tend to hydrolyze to a hydrated Pu-oxide precipitate. The precipitate is too dense to agitate well with a motor-driven stirrer; it tends to be pushed into a pile at the beaker walls. Furthermore, if the stirrer

contacts the shavings directly, it is possible to slosh the liquid out of the beaker. For this reason, it is best not to use a motor-driven stirrer until the metal shavings have been converted to the hydrated precipitate.

The plastic spatula may be used periodically to agitate the solution or to disperse the dense precipitate.

In order to speed up the filtration process after the washing steps, it is desirable to leave as much precipitate in the beaker as possible. The longer the precipitate settles, the less Pu-carryover there is during filtration. (The precipitate will settle overnight into a dense bed, which can be decanted onto a filter with little Pu carryover.) The use of plastic filtration units with membrane filters is convenient when filtering samples after brief settling times. Even when ~100 g of precipitate carries over, one liter of solution will filter through a membrane filter unit in 15 minutes or less. Under the same conditions, filtration through a Whatman #42 paper filter might take several hours. It is easy to wash the precipitate from the membrane filter unit back into the beaker with a stream of water. The filter unit may be reused multiple times.

After all washes are finished, it is necessary to transfer the Pu to a paper filter for calcination. Although the treatment of the 200 g batch was successful, it was difficult to manage the transfer of the Pu precipitate to the calcining crucible on a 10 cm paper filter with this quantity of material. Therefore, we recommend keeping batch sizes near 100 g.

Reagents

40 wt% NH_4F : Dissolve 885 g NH_4F in 1330 g distilled or deionized water. Filter the solution through a Whatman #42 filter paper or a 0.45 μm membrane filter. Transfer the solution to a 2 liter polyethylene storage bottle. (The density of 40% NH_4F is ~1.11 g/mL.)

5 wt% NH_4F : Mix 250 g of 40% NH_4F solution with 1750 g distilled or deionized water in a 2 liter polyethylene storage bottle.

General Procedure

Anyone using this procedure should perform site-specific safety analyses and adjust the procedure accordingly to meet the applicable safety basis documentation.

The procedure below assumes that 500 mL of water will be combined with 500 mL of 40 wt% NH_4F during a treatment to produce one liter of ~20 wt% NH_4F , which will dissolve a maximum of 13 g of Be. Each batch is treated one additional time more than the number of estimated treatments to ensure that all the Be is dissolved. Therefore, 1-13 g Be is treated twice; 14-26 g Be three times; 27-39 g Be four times, and so on.

The liquid amounts may be scaled accordingly for larger or smaller beakers. Keeping the liquid level in the beaker below half full is recommended. **The beaker should not be filled more than two thirds full.**

It is good practice to monitor neutron dose rates before and during treatment. However, once the water is added to the sample, the $^9\text{Be}(\alpha, n)^{12}\text{C}$ neutron dose rates generally are insignificant, since the alpha particles are stopped in the water.

Prepare the sample.

- Weigh the sample into the 3-liter beaker. It is not necessary to cut machine turnings/shavings into short strips.
- Calculate the maximum amount of Be possible from the difference between the net weight and the Pu element weight, in order to decide how many treatments are necessary.

Dissolve the Be.

- Cover the sample with 500 mL of water.
- With the hot plate off, add 500 ml of 40 wt% NH_4F in 20 mL increments, according to the rate of hydrogen evolution. **Do not add additional increments unless the foamy head is less than ~2 inches.** It generally takes about 1 hour to add the 40 wt% NH_4F .

Beryllium dissolution is usually obvious after the second addition of 40 wt% NH_4F . Even when there is no beryllium to dissolve, intermittent bubbles can form from the slow conversion of Pu metal to the hydrated Pu-oxide. However, it is relatively easy to recognize true Be dissolution, since it is accompanied by significant warming, and hydrogen evolution across the entire surface of the solution.

The rate of addition should be controlled to prevent the solution temperature from exceeding 70°C. As the solution heats from the exothermic reaction, the walls of the beaker become coated with condensation, and “steam” can be observed above the solution. These symptoms indicate when thermocouple measurements of the temperature become necessary.

- Use the hot plate to keep the solution in the 50-60°C range if the reaction heat is insufficient. Keep the solution in this range for 30 minutes after the addition of 500 mL of 40 wt% NH_4F is complete.

The motorized stirrer may be used if care is taken that turnings are not caught on the propeller. It is good practice to agitate the precipitate with the spatula periodically.

- Turn off the hot plate and stirrer after 30 minutes. Raise the propeller out of the solution and rinse any precipitate off the blades with water.

Filter the supernate.

- Filter the supernate when the solution has cooled enough for easy handling, leaving as much precipitate in the beaker as possible.
- After the filtration is finished, rinse any Pu on the filter back into the beaker.

If more treatments are necessary, repeat the Be dissolution and filtration steps above.

If the Be dissolution is finished, wash the precipitate as follows.

- Wash the Pu precipitate in the beaker with ~250 mL of 5 wt% NH_4F . Use the spatula to agitate the precipitate briefly.

- When the precipitate has settled, filter the wash, leaving as much Pu in the beaker as possible.
- After the filtration is finished, rinse any Pu on the filter back into the beaker.
- Repeat the wash/filtration twice more with ~250 mL of 5 wt% NH_4F .
- Wash and filter the Pu twice with ~250 mL deionized or distilled water in the beaker.
- Transfer the Pu to a Whatman #42 paper filter with a third wash using ~250 mL water.
- Dry the precipitate overnight by continuing to apply vacuum to the filter.

Calcine the Pu, and solidify the liquid waste as in Reference 1.

References

¹ O. H. Krikorian and F. G. Bajao; UCRL-TR-207845, 2004, 8p.

² C. J. Hardy and D. Scargill; *J. Chem. Soc*, 1961, 2658-63.

³ H. J. Whitfield; ; AAEC/TM137, 1962, 9p.